



Steam reforming of biomass-derived organics: Interactions of different mixture components on Ni/Al₂O₃ based catalysts

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ABSTRACT

The reaction of steam with ethanol, ethanol + phenol, ethanol + phenol + tetrahydrothiophene, methanol + phenol, methanol + naphthalene and methanol + phenol + naphthalene mixtures in the vapour phase has been studied over catalysts based on Ni/Al₂O₃. The main conclusion is that Ni-alumina based steam reforming catalysts are effective for steam reforming of phenol and naphthalene even mixed each other and with light alcohols at T > 973 K in the absence of sulphur. However, at lower temperatures and when deactivated by sulphur they may become active catalysts in converting these molecules in a number of polyalkylphenols which represent low-volatility secondary and tertiary tars.

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1. Introduction

The co-production of tars, i.e. mixtures of quite heavy molecules whose vapor pollutes the produced gases, is a main drawback of some biomass conversion technologies, such as gasification and pyrolysis [1,2], still limiting their development at the industrial scale [3,4]. The catalytic steam reforming of tars [5,6] either performed in the same gasifier or in a secondary step, is considered to be a promising technique to resolve this problem [7]. Ni-based catalysts have been found to be active in converting real biomass tars [8–12] and are also commercialized for this application [13], but they need high reaction temperatures (>1073 K) to reduce issues arising from coking and sulfur poisoning. Noble metal containing catalysts, such as Rh-based ones [11,14] are more active and more resistant to deactivation. Thus, they may be useful for lower temperature application. However, depending on the process configuration, working at lower temperature might not be practical, taking into account that gasification usually occurs above 1073 K.

Additionally, it must be taken into account that real tars may be very complex mixtures, where lighter molecules may be present together with heavier ones [15]. According to Aigner et al. [16] primary tar products coming from cellulose and hemicellulose are constituted by alcohols, ketones, aldehydes and carboxylic acids, while those coming from lignin are phenols and other mononuclear aromatics. Secondary tars, such as alkylated mono- and di-aromatics, including heterocyclics, form at higher temperature by conversion of primary tars (T > 773 K). Tertiary tars form at T > 1073 K and are mainly constituted by mono and polynuclear aromatic hydrocarbons such as benzene, naphthalenes, phenantrenes, pyrene and benzopyrene. In practice, depending on the process (gasification, pyrolysis), on the reactor conditions, on the biomass raw material and on the operational parameters, tars composition may differ significantly [16,17]. In parallel, also the working conditions of the steam reforming catalyst bed may differ in terms of temperature, amount of steam, real temperature, amount of poisons, etc. and may also fluctuate over time.

Although several studies report on the conversion of real biomass tars [8–11], most of the literature concerns the conversion of model molecules, usually benzene, phenol or naphthalene [11]. Studies focusing the interaction between different tar molecules over steam reforming catalysts are lacking. Using ethanol-phenol mixtures as models for tar, it has been shown that indeed at

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moderate temperatures such molecules can react together over steam reforming catalysts, producing (poly) alkylphenols [18]. At least part of this chemistry may occur on the catalyst support surface. Thus, in particular during non-stationary conditions (such as during start-up and shut-down procedures), or when catalysis is performed at lower temperatures, the quality of the gases can be even worsened by contact with the steam reforming catalyst.

Steam reforming over Ni-based catalysts is also being considered for the production of hydrogen from other biomass-derived flows such as bioethanol [19–29] and pyrolysis bio-oils [30,31]. Also in this case the real mixtures are quite complex: several organic impurities and sulphur compounds are or may be in fact present in real bioethanol [32,33], while bio-oils are mixtures of hundreds of components, including low and high molecular weight oxygenated compounds, such as carboxylic acids, aldehydes, ketones, alcohols and phenols [34]. Also for these applications, most published studies use pure molecules (pure ethanol, phenol, acetic acid) thus neglecting the possible interactions between compounds.

To go deeper in our studies, we substituted methanol for ethanol. In fact, methanol is a typical product of lignin pyrolysis and is reported to be present in biomass treating gases in significant amounts [15,16]. Additionally, we compared phenol and naphthalene conversion, as two most typical tar molecules. Finally, we mixed methanol, phenol and naphthalene, to look whether their reactivity is mutually influenced. We used catalysts constituted by Ni/ γ -Al₂O₃ using a pure γ -Al₂O₃ support and a silica-containing alumina support, which have been the object of previous characterization studies [35]. The presence of silica only slightly modifies the performances of the catalysts.

2. Experimental

2.1. Materials preparation

Catalysts have been prepared [35] by wet impregnation of a pure γ -Al₂O₃ support (Puralox Sba 200 from Sasol) or a 5% SiO₂-containing γ -Al₂O₃ support (Siralox 5/170 from Sasol) using Ni(NO₃)₂·6H₂O water solution as precursor. After impregnation, drying at 363 K for 5 h has been performed. Final calcination has been performed at 973 K, 1023 K or 1073 K. The sample notation reports the amount of Ni deposited on the support (% wt_{Ni}/wt_{support}), the support (Puralox = P; Siralox = S) and the final calcination temperature in Celsius degrees. As an example, Ni16S700 contains 16% Ni on Siralox and has been calcined at 973 K (700 °C).

2.2. Raman study

A Renishaw Raman System 2000 spectrometer with a He-Ne laser (632.8 nm) excitation source and equipped with a Peltier Cooled CCD as detector and a Leica Optical Microscope was used. Different parameters were optimised for this analysis, i.e. laser power, magnification and accumulations.

2.3. Catalytic experiments

The catalytic experiments were carried out in a fixed-bed tubular silica glass flow reactor, operating isothermally. The reactor was loaded with the catalyst mixed with 440 mg of silica glass particles (60–70 mesh sieved). No catalyst pretreatments were performed. Single phase liquid solutions were pumped through a HPLC pump (Shimadzu Corp. LC-D10 AD) in an appropriate heating section at 583 K of the feed line to produce gaseous mixtures in the He inert carrier.

Reactor oven temperature was varied from in steps waiting for steady state conditions before product analysis. The measured bed

temperatures were usually slightly lower than the furnace temperatures according to the whole endothermicity of the reactions.

Products analyses were performed with a gas-chromatograph Agilent 4890 equipped with a Varian capillary column “Molsieve 5A/Porabond Q Tandem” and TCD and FID detectors in series. Between them, a Nickel Catalyst Tube was employed to hydrogenate CO and CO₂ to CH₄. Products analysis was also performed with a GC/MS (ThermoFisher), in order to have a precise identification of the involved compounds. Hydrogen molar amounts were measured using the negative peak in the GC-TCD detector and confirmed by the molar balances of the other compounds.

Reactants conversion is defined as follows:

$$X_{\text{reactant}} = \frac{n_{\text{react.in}} - n_{\text{react.out}}}{n_{\text{react.in}}} \quad (1)$$

Selectivities to the single C-containing products S_i^E , S_i^P and S_i^T , (i refers to a product molecule) were calculated with respect to single reactants conversion (E, P mean ethanol, phenol) or with respect to the total carbon reactant conversion (T), using the formulas:

$$S_i^E = \frac{n_i}{v_i^E (n_{\text{in}}^E - n_{\text{out}}^E)} \quad (2)$$

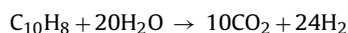
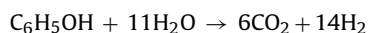
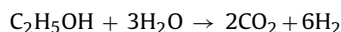
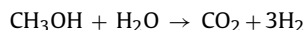
$$S_i^P = \frac{n_i}{v_i^P (n_{\text{in}}^P - n_{\text{out}}^P)} \quad (3)$$

$$S_i^T = \frac{n_i}{v_i (n_{\text{in}}^T - n_{\text{out}}^T)} \quad (4)$$

where n_i is the moles number of compound i, and v_i is the ratio of stoichiometric reaction coefficients, n^E and n^P are ethanol and phenol moles at the inlet and at the outlet of the reactor.

When applied to the overall carbon feed, n_i is the carbon moles number of compound i, n^T is the carbon moles number of reactants mixture as a whole and $v_i = 1$.

Hydrogen yield is defined as the molar percentage of hydrogen produced with respect to the maximum hydrogen that could be produced through steam reforming reactions:



i.e. 3 hydrogen molecules for each methanol molecule fed, 6 for ethanol, 14 hydrogen molecule for phenol, 24 hydrogen molecules for naphthalene.

2.3.1. Ethanol and ethanol-phenol steam reforming experiment

For the experiments concerning ethanol steam reforming two different tests were carried out with different reactant partial pressure but with comparable space velocities. In one case, the reactor was loaded with 44 mg of catalyst. The feed was constituted by a mixture of ethanol and water with a molar ratio (water to ethanol) equal to 6 in He (41.6% mol/mol), thus giving rise to a Gas Hourly Space Velocity equal to GHSV = 51700 h⁻¹. In the other case, the reactor was loaded with 88 mg of catalysts. The feed was constituted by a mixture of ethanol and water with a molar ratio (water to ethanol) equal to 6 in He (72.1% mol/mol) added as carrier gas, thus giving rise to a Gas Hourly Space Velocity equal to GHSV = 54000 h⁻¹. The reaction temperature was varied in-between 523 and 1023 K.

For ethanol-phenol steam reforming (GHSV = 54000 h⁻¹) the gaseous mixture had the following composition: 39.3% He, 54.6%

water, 4.1% ethanol and 2% phenol mol/mol. Reactor oven temperature was varied from 773 K to 1023 K, and vice-versa.

To investigate sulphur poisoning, two sequential pulses tetrahydrothiophene (THT), equal to 0.011 mol_S/mol_{Ni} and after 0.033 mol_S/mol_{Ni}, and then a further stay in sulphur free stream were performed. In this case, the temperature was kept constant for the entire experiment at 973 K and 873 K respectively and THT has been pulsed injecting, with a syringe, the corresponding quantity of liquid in the preheating zone.

2.3.2. Methanol-phenol, methanol-naphthalene and-methanol phenol naphthalene steam reforming experiments

In all these cases, 88 mg catalyst were used. For methanol/phenol steam reforming experiments, the following gas phase composition was fed (% v/v) 0.5% phenol, 9.6% methanol, 16.5% water, 73.4% He (as carrier gas) with a total flow of 70 Nml/min and a GHSV = 48000 h⁻¹. In the case of methanol-naphthalene steam reforming experiments, the gas composition used was 79.2% He, 10.9% H₂O, 9.9% CH₃OH and 145 ppm of C₁₀H₈ with a total flow of 75 Nml/min and a GHSV = 50000 h⁻¹. For methanol-phenol-naphthalene steam reforming experiments, the following composition was fed: 0.5% phenol, 9.54% methanol, 16.4% H₂O, 73.6% He and 168 ppm of naphthalene. Accordingly, the obtained GHSV was equal to 48000 h⁻¹.

The reaction temperature was varied in-between 773 K to 1073 K.

2.4. Thermodynamic calculations

Thermodynamic calculations were performed using the minimization of the Gibbs free energy method (Gibbs reactor), considering the same feed compositions and flows applied experimentally. The Redlich-Kwong-Soave equation of state (RKS) was used.

3. Results and discussion

3.1. Ethanol/steam conversion

In Fig. 1 the results concerning the activity of the Ni16S700 catalyst in ethanol/steam conversion, by feeding 8.1% ethanol, 50.3% water and 41.6% He, are reported as a function of the reaction temperature. Conversion of ethanol starts to be significant near 573 K and is complete at 773 K but conversion of water is negative in this temperature range, i.e. water is produced during the reaction. In fact, the products in this temperature range are acetaldehyde coming by ethanol dehydrogenation reaction as well as diethylether and ethylene produced by ethanol dehydration. Some acetone is produced too. At 873 K and above, water conversion starts to be positive and CO and CO₂ start to be formed together with some methane, showing the typical products of ethanol steam reforming. The best hydrogen yield is obtained at 973 K, 63%. In Table 1 the experimental product distribution is compared with that calculated based on thermodynamics in our pressure and feed conditions, at 973 K. The data show that we obtain an excess of CH₄ and CO, with respect to thermodynamic equilibrium. This suggests that CH₄ is formed from a way different from methanation. In fact, it seems likely that methane is mainly produced on Ni catalysts by decomposition reactions, Ni catalysts being active in the decomposition of ethanol itself [36,37]:



maybe occurring in two steps, after previous dehydrogenation to acetaldehyde.

From these data, it is evident that this 16% Ni/Al₂O₃ catalyst is actually active as a steam reforming catalyst for ethanol at least at

973 K but the hydrogen yield is limited by the formation of methane (12% selectivity) and CO, instead of CO₂ which is the final expected product of steam reforming reaction.

The catalytic activity of Ni16S700 is definitely lower than that of more charged catalysts such as Ni39S700, as discussed elsewhere [35] and Ni125S700 [36].

In Fig. 2 we report the data, obtained with the same catalyst, the same water-to-ethanol feed ratio and the same contact time, but reducing the total reactants partial pressure. At low temperature (573 K) the main products are acetaldehyde and diethylether, while by increasing temperature, ethanol dehydration to ethylene becomes the main reaction until 873 K. At 973 K, ethanol steam reforming starts with CO as the main C-product together with methane and CO₂. The best performances are obtained at 1023 K where H₂ yield approaches 83% with no coproduction of methane. This suggests that ethanol decomposition rate is strongly reduced by lowering ethanol partial pressure.

In Fig. 3, the results of the experiment performed on the Ni16P750 catalyst in the same conditions used for Ni16S700 in Fig. 1's experiment. In this case, the experiment is performed by descending reaction temperature, using a catalyst that has been conditioned in reaction conditions at high temperature (1023 K). Indeed the catalyst fully converts ethanol to CO_x + H₂, essentially with no methane formation at 973 K. As shown in Table 1, in this experiment equilibrium is closely approached. However, the lack of CH₄ production allows to increase H₂ yield. By decreasing reaction temperature to 873 K, ethanol steam reforming is still largely predominant, but methane appears (8%). This behavior suggests that the ethanol decomposition reaction (1) has a lower activation energy than steam reforming reaction, whose rate is likely dominated by the energy need for water activation. At even lower temperature steam reforming almost vanishes and ethylene becomes the largely predominant product (63% at 773 K). Finally the conversion drops and ethanol dehydration to diethylether is the main reaction. At 523 K also dehydrogenation to acetaldehyde is observed.

3.2. Ethanol/phenol/steam conversion

In Fig. 4, the results concerning the conversion of ethanol/phenol mixture over the Ni16S700 and Ni16P750 catalysts in similar conditions are reported. In the upper sections of Fig. 4 ethanol conversion and the selectivities to products assumed to come from ethanol, calculated with respect to converted ethanol, are reported. In the lower section we report the conversion of phenol and the selectivities to products assumed to come from phenol, calculated with respect to converted phenol. At 773 K, ethanol conversion is very high (98%) while that of phenol is quite low (27%). Ethanol converts essentially to ethylene and, to a lower extent, to acetaldehyde at 773 K, as occurs the absence of phenol. Additionally, part of ethanol reacts with phenol producing mainly C₈ monoalkylated phenols and C₁₀ dialkylated phenols. Some benzene is also observed, supposed to come from phenol hydrodeoxygenation, using hydrogen coming from ethanol dehydrogenation to acetaldehyde. Steam reforming neither of phenol nor of ethanol occurs to a significant extent.

Over both catalysts at 873 K steam reforming of both ethanol and phenol starts to occur producing CO and CO₂. In parallel, selectivities to ethylene, acetaldehyde and alkylphenols decrease. At 973 K steam reforming only is observed. Both ethanol and phenol are almost fully converted into CO and CO₂, with very high yields in hydrogen (80%). These data show that, in spite of the relatively low Ni loading, these catalysts allow (in the absence of sulphur) to fully convert both phenol and ethanol to syngas at 973 K.

The results described in Figs. 1 and 4 are comparable in terms of reaction conditions. Thus, the comparison of the data obtained in

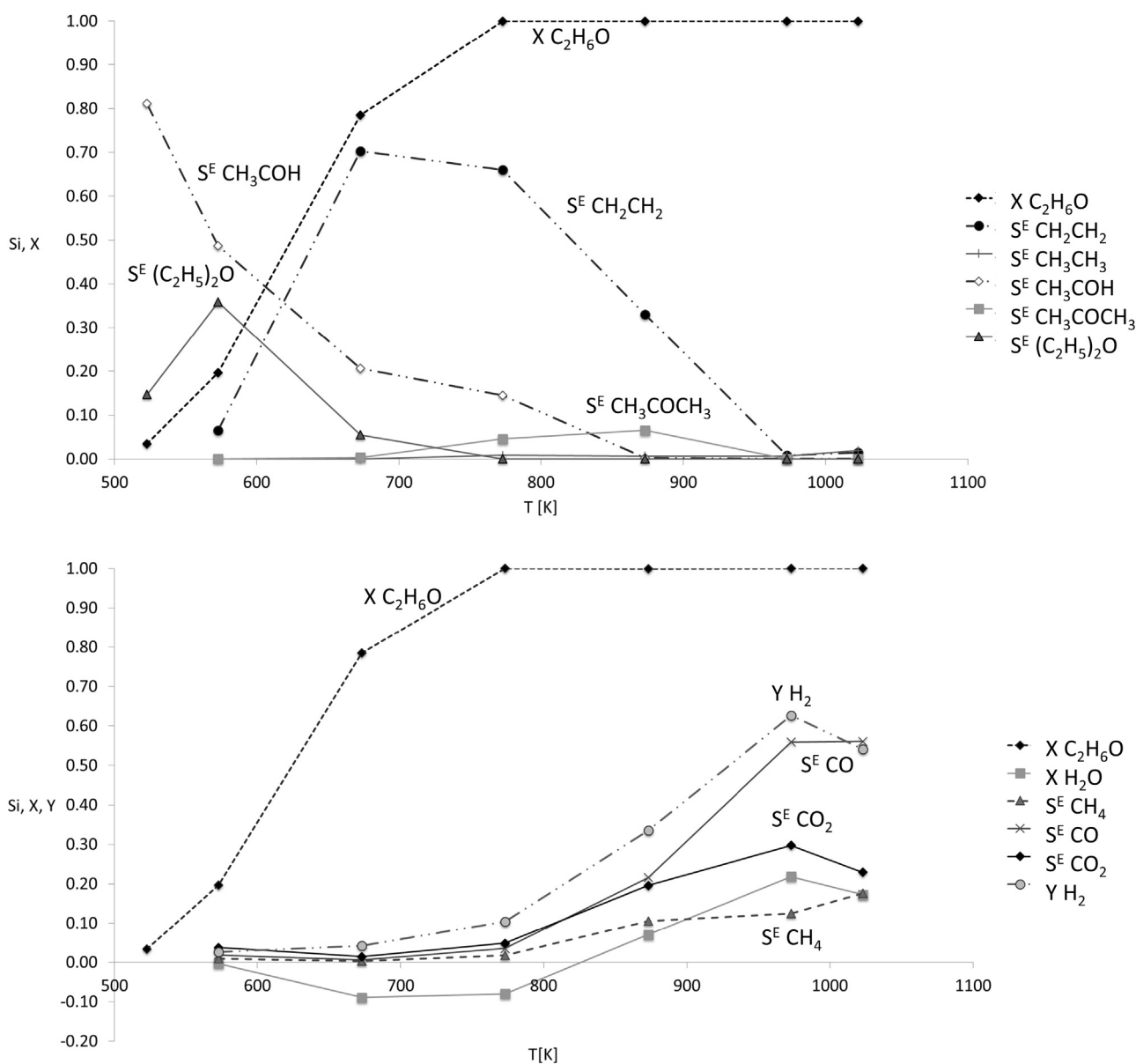


Fig. 1. Conversions, selectivities to carbon products (S_i) and hydrogen yield (Y_{H_2}) obtained in ESR as a function of temperature on Ni16S700 at high reactant partial pressures.

Table 1

Experimental and theoretical molar product distributions at 973 K.

Components	Thermodynamic Ethanol SR (high reactant partial pressure)	Experimental Ethanol SR (high reactant partial pressure) Ni16S700	Experimental Ethanol SR (high reactant partial pressure) Ni16P750	Thermodynamic Ethanol-phenol SR	Experimental Ethanol-phenol SR (Ni16S700)	Experimental Ethanol-phenol SR (Ni16P750)
CH ₄	0.001	0.016	0.001	0.001	0.001	0.000
CO	0.057	0.072	0.044	0.074	0.054	0.059
CO ₂	0.068	0.039	0.079	0.078	0.088	0.087
CH ₂ CH ₂	0.000	0.001	0.000	0.000	0.000	0.000
CH ₃ CH ₃	0.000	0.001	0.000	0.000	0.000	0.000
CH ₃ CHO	0.000	0.000	0.000	0.000	0.003	0.000
C ₂ H ₆ O	0.000	0.000	0.000	0.000	0.001	0.000
C ₆ H ₆	0.000	0.000	0.000	0.000	0.000	0.000
C ₆ H ₆ O	–	–	–	0.000	0.001	0.000
H ₂	0.315	0.244	0.325	0.321	0.315	0.320
H ₂ O	0.247	0.304	0.231	0.229	0.235	0.205
He	0.313	0.323	0.321	0.297	0.303	0.329
C ₈	–	–	–	0.000	0.000	0.000
	1.000	1.000	1.000	1.000	1.000	1.000

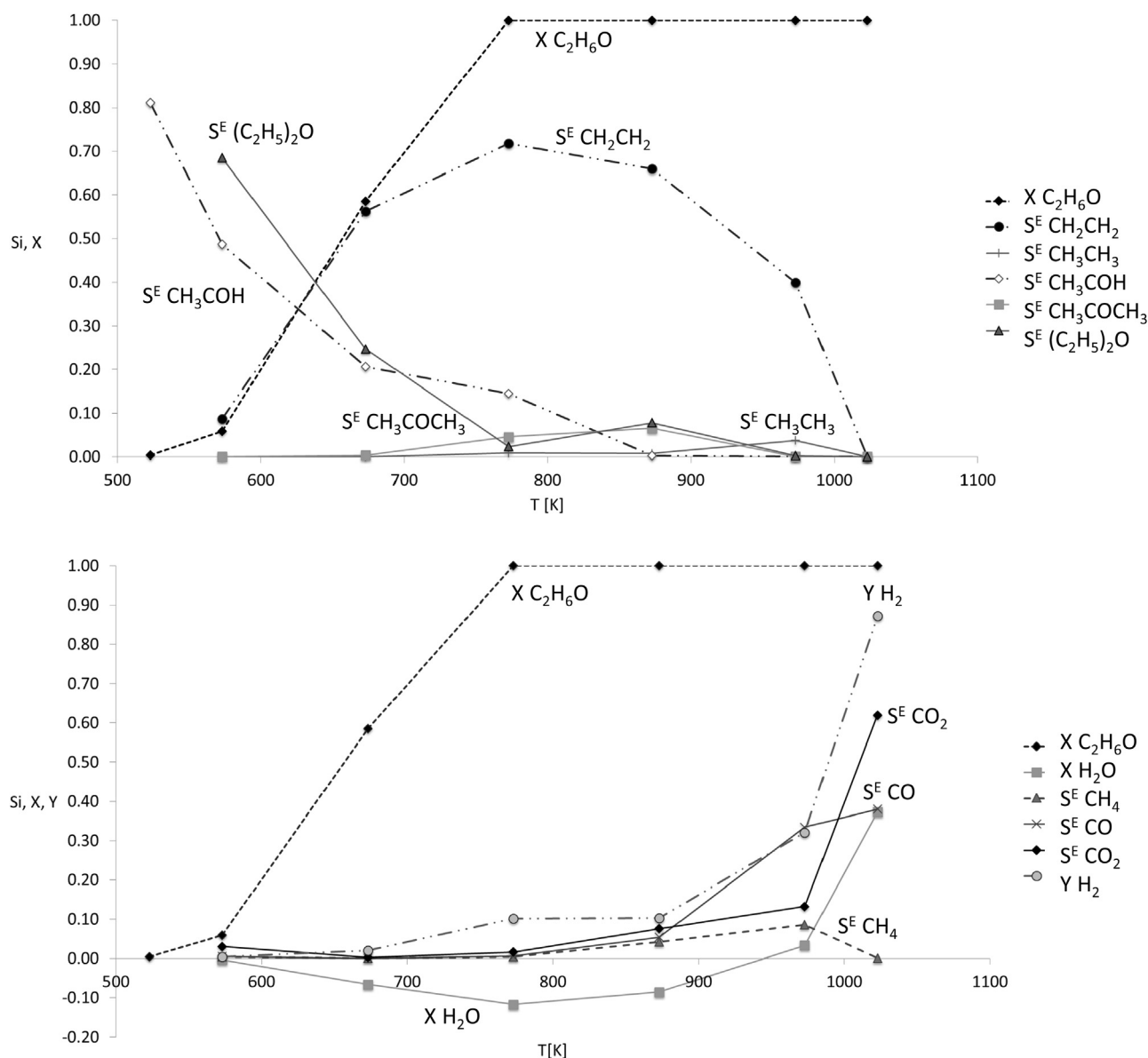


Fig. 2. Conversions, selectivities to carbon products (S_i) and hydrogen yield (Y_{H_2}) obtained in ESR as a function of temperature on Ni16S700 at low reactant partial pressures (dilute conditions).

the absence and in the presence of phenol can be taken as indicative of the effect of such an additional compound in ethanol conversion in the presence of steam. In spite of offering the possibility of a new reaction (the alkylation), the presence of phenol results in a lowering of the conversion of ethanol at both 773 and 873 K, i.e. in conditions where dehydration is the main path of ethanol conversion and steam reforming still is not occurring extensively. At 773 K the presence of phenol causes apparently only a slight decrease in ethanol conversion (from 100% to 98%) but product selectivities (calculated with respect to ethanol) are essentially constant (65% to ethylene, 16% to acetaldehyde) with alkylates substituting for acetone. At 873 K the presence of phenol causes a larger decrease in ethanol conversion (from 100% to 86%) with a significant increase in ethylene selectivity (from 33 to 50%) and, even more, in acetaldehyde selectivity (from 0% to 16%), and a strong decrease in ethanol steam reforming selectivity (from 42% to 13% as $S^E_{(\text{CO}+\text{CO}_2)}$). It is evident that at 873 K phenol actually inhibits significantly ethanol steam reforming, shifting partially the reactivity of ethanol towards dehydration and dehydrogenation. Instead,

at 973 K and 1023 K, when conversion is complete both with and without phenol, the formation of methane is strongly reduced in the presence of phenol and the hydrogen yield strongly increased from 63% to a value higher than 80%. In Table 1 the experimental product composition is compared with that calculated on the base of thermodynamics. In this case, the produced methane is in line with the thermodynamic forecast, while CO_2 is produced in excess again with respect to the thermodynamic value, at the expense of CO, as usually found [18]. This confirms that CO_2 is not formed by conversion of gas phase CO (water gas shift), while gas phase CO could be produced by reverse water gas shift and/or from an independent way (formation on the surface from the reactants and desorption). Hydrogen production is slightly lower than the thermodynamic value due to the amounts of unconverted ethanol and acetaldehyde.

In Fig. 4 the catalytic results obtained with the Ni16P750 catalyst in the conversion of ethanol/phenol mixture after conditioning are also reported. These data can be compared with those reported in Fig. 3 for ethanol/steam conversion over the same catalyst. Also

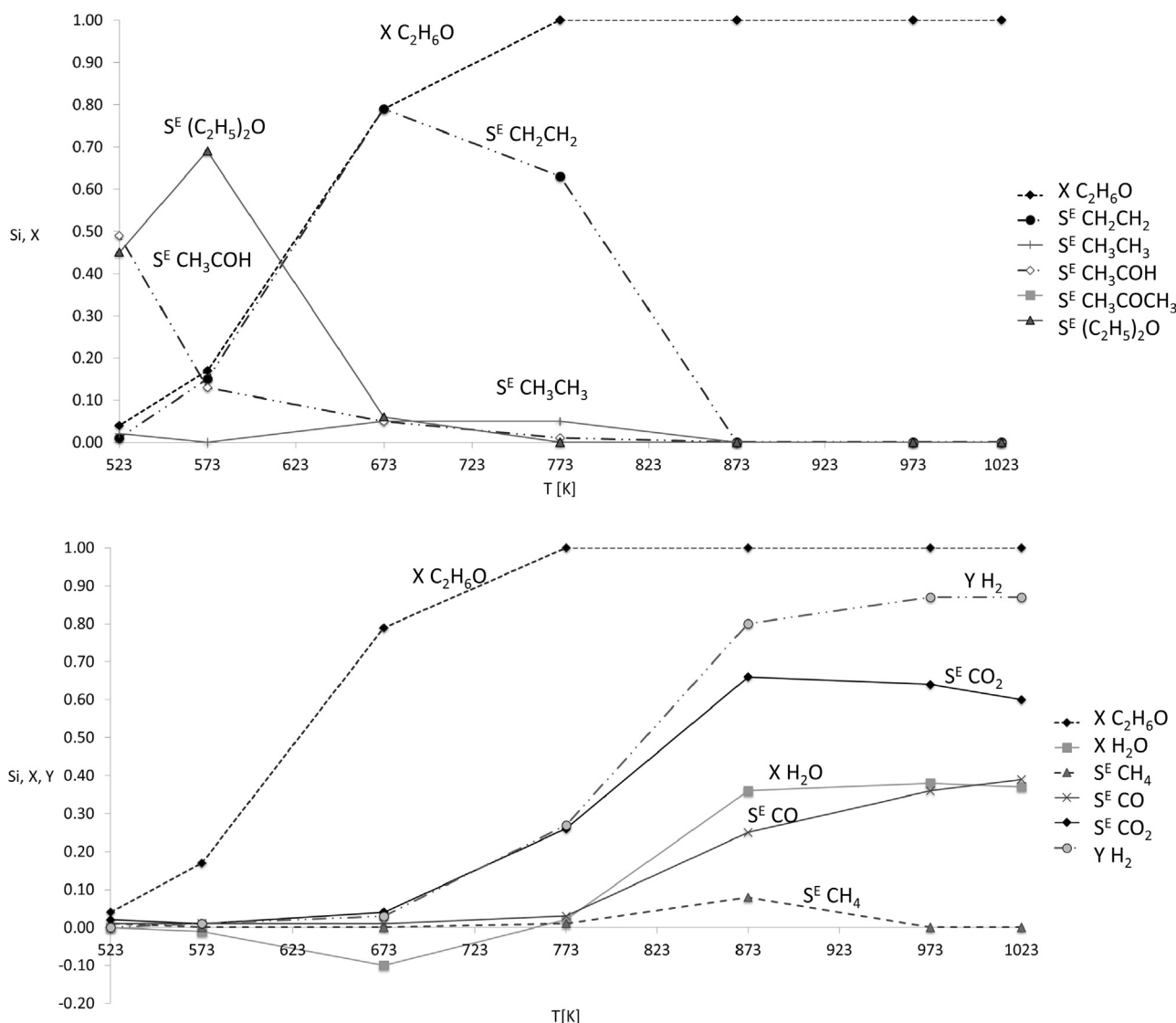


Fig. 3. Conversions, selectivities to carbon products (S_i) and hydrogen yield (Y_{H_2}) obtained in ESR as a function of temperature on Ni16P750 at high reactant partial pressures after on stream conditioning in decreasing temperature experiment.

in this case the presence of phenol at 873 K favours conversion of ethanol to ethylene, while at 773 K definitely inhibits ethanol conversion and results in C₈ alkylation products.

As already reported [38], and shown above, at low phenol conversion and temperature the alkylation of phenol occurs. As said, the main products are *ortho*- and *para*-ethylphenol and some 2,4-diethylphenols. However, a number of other compounds are observed in the same conditions, although with low concentration. The structures of the phenol conversion products revealed by GC–MS are reported in Fig. 5. Interestingly, exclusively C-alkylation is observed, with no O-alkylation. On the other hand, a number of very heavy compounds is observed, up to C₁₄ compounds. Most of these compounds have very low volatility and may be classified as secondary or tertiary tars. They form over the steam reforming catalyst when temperature is low and steam reforming still does not occur. The alkylation essentially occurs at 773–873 K vanishing at higher temperatures. Alkylation is more abundant for low-Ni-loading catalysts and increases also upon sulphur deactivation of steam reforming. This suggests that this chemistry implies the alumina support where isolated Ni ions are deposited.

In Fig. 6, the product composition during the steam reforming of ethanol + phenol at 973 K is reported as an effect of time on

stream up to near 700 min. The outlet flow composition calculated at thermodynamic equilibrium is reported. It is quite evident that the catalytic behavior is rather stable and that the product composition is very near the thermodynamic equilibrium, considering experimental error. Hydrogen yield is a little lower than thermodynamics due to the presence of small amounts of methane that, in these conditions, should be almost completely steam reformed. This is however partially compensated, at least at low times on stream, by the slightly higher CO₂ concentration and the slightly lower CO concentration observed with respect to thermodynamics. This further supports the idea that CO₂ is the primary gaseous product in our conditions, CO being produced by reverse water gas shift or by ethanol decomposition parallel path. Interestingly, however, at longer times on stream the CO₂ and CO concentrations change a little, being now corresponding to the equilibrium values, within experimental error. This suggests that, by increasing time on stream, the catalyst is activated also with respect to reverse water gas shift reaction. In any case it is quite evident that there is no trace of deactivation during our 700 min experiment.

After the above experiment, the catalyst has been analyzed by Raman spectroscopy. The spectrum of the catalyst, reported in

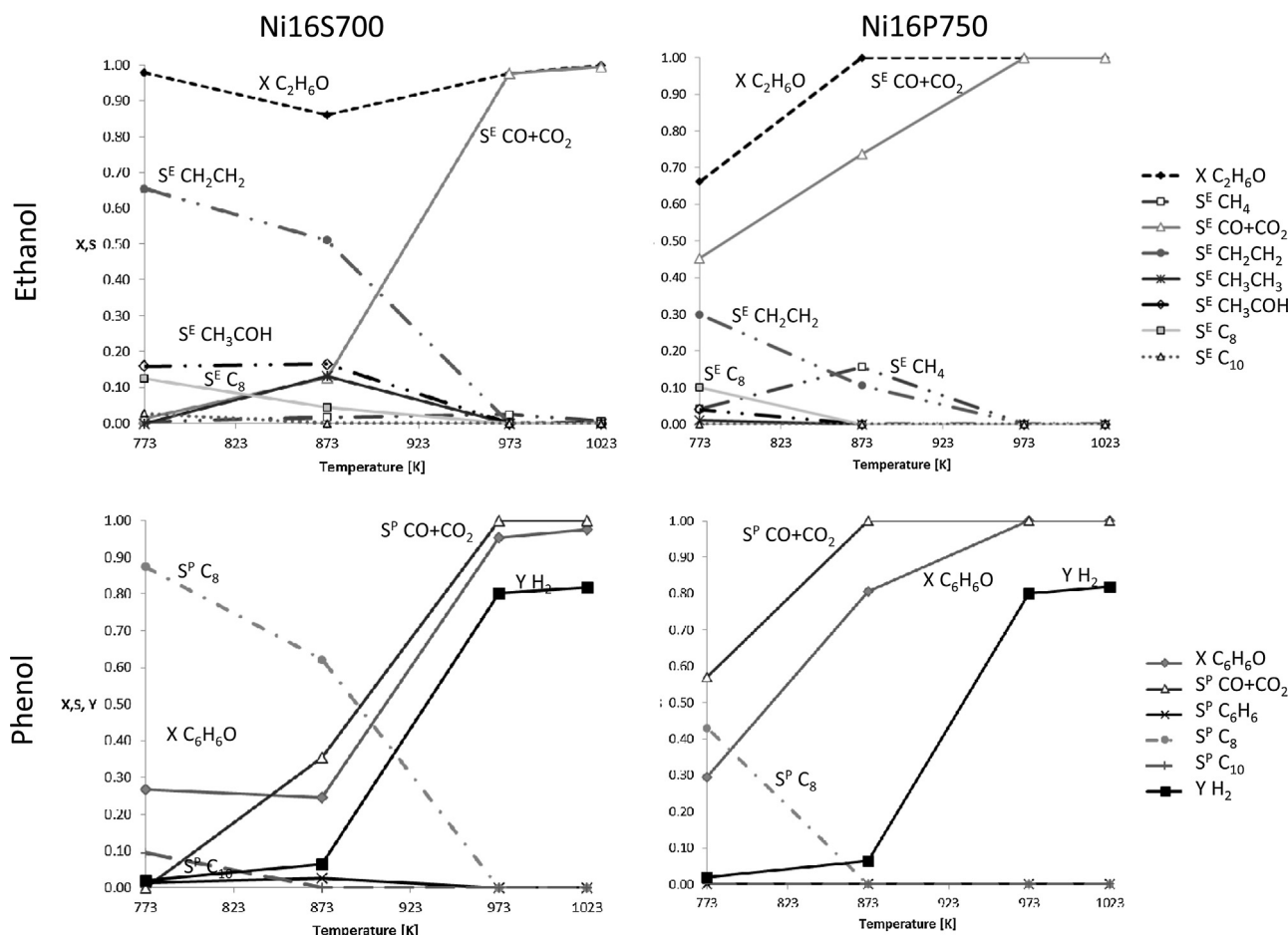


Fig. 4. Conversions, selectivities to carbon products (S_i) (with respect to ethanol and phenol respectively) and hydrogen yield (Y_{H_2}) obtained in ethanol-phenol mixture conversion as a function of temperature on (left) Ni16S700 in increasing temperature experiment and (right) Ni16P750 in decreasing temperature mode.

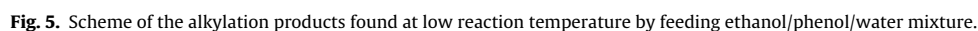
Fig. 7, shows the formation, during the reaction, of two strong Raman peaks at 1326 and 1593 cm^{-1} , together with three much weaker components at ca 3180 , 2900 and 2630 cm^{-1} that are likely the harmonics of the above main peaks (the overtones with the combination in the middle). The main bands are usually denoted as D and G band. The bigger intensity of the D band and the lack of splitting of the higher frequency main band is indicative of the formation of a disordered graphite-like structure [39] more than of multi-walled [40] or single-wall [41] carbon nanotubes. These data show that indeed some deposition of carbonaceous material occurred during the experiment although still deactivation has not been detected and pressure drops were not observed.

3.3. Ethanol/phenol/tetrahydrothiophene/steam conversion

In Fig. 8, the behavior of the Ni16S700 catalyst in the conversion of the ethanol + phenol mixture in the presence of steam and tetrahydrothiophene (THT), as a source of sulphur, is reported, at 973 K (left side) and at 873 K (right side). At 973 K in the absence of THT the conversion of both organic reactants is definitely high while that of water (which is in large stoichiometric excess) is near 50%. The injection of $36.3\text{ }\mu\text{g}_\text{S}$, corresponding to $0.011\text{ mol}_\text{S}/\text{mol}_\text{Ni}$, to the normal feed (performed 30 min before the product analysis) does not cause significant changes to the catalytic behavior of the catalyst but the further addition of $109\text{ }\mu\text{g}_\text{S}$ (additional

$0.033\text{ mol}_\text{S}/\text{mol}_\text{Ni}$) causes an evident deactivation. Interestingly the total sulphur injected ($0.044\text{ mol}_\text{S}/\text{mol}_\text{Ni}$) is still much lower than that needed to convert Ni into NiS. While ethanol conversion is weakly affected, phenol conversion drops to 19%, and water conversion drops to zero. Accordingly, ethylene and acetaldehyde selectivities jump from zero to more than 50% and 18%, respectively. Also methane selectivity grows. Further stay on sulphur-free stream causes recovering of the full conversion of both organic reactants but the conversion of water is un-completely recovered according to a definitely increased selectivity to CO and reduced selectivity to CO_2 and hydrogen yield.

The same experiment performed at 873 K gives rise to quite different results. We have to remind that, at this temperature, conversion of the reactants is still un-complete and steam reforming occurs to a small extent, already in the absence of sulphur. In fact ethylene and acetaldehyde are the main reaction products while CO and CO_2 selectivities are near 20% each. The three reactant conversions are definitely reduced after the first injection and, even more, after the second injection, and they are not recovered after staying in S-free stream. Selectivities to steam reforming products decrease just after the first injection in favor of selectivity to ethylene and acetaldehyde, while also phenol alkylation to ethylphenols is observed again. Steam reforming products selectivities are quite stable after the second injection, and slightly recovered by staying in the S-free stream.



T Furnace [K]	C Conversion	X CH ₄ O	X C ₆ H ₆ O	X H ₂ O	Y H ₂	S CH ₄	S CO	S CO ₂	S C ₂ H ₄	S C ₂ H ₆ O (DME)	S CH ₂ O	S C ₄	S C ₇	S C ₁₂
773	0.85	0.81	1.00	-0.31	0.07	0.12	0.14	0.06	0.02	0.11	0.00	0.02	0.00	0.53
873	0.13	0.12	0.14	-0.01	0.05	0.08	0.23	0.11	0.00	0.13	0.16	0.00	0.29	0.00
973	0.73	0.68	0.89	0.39	0.59	0.00	0.52	0.48	0.00	0.00	0.00	0.00	0.00	0.00
1023	1.00	1.00	1.00	0.48	0.80	0.00	0.56	0.44	0.00	0.00	0.00	0.00	0.00	0.00
1073	1.00	1.00	1.00	0.45	0.79	0.00	0.59	0.41	0.00	0.00	0.00	0.00	0.00	0.00

The experiments of conversion of methanol and phenol in the presence of steam have been performed on the Ni16P800 and Ni39P800 catalysts and the results are reported in [Tables 2 and 3](#)

Over Ni16P800 at 773 K methanol and phenol react largely each other producing hexamethyl-benzene, with 98% yield with respect to phenol. By increasing the reaction temperature to 873 K, this reaction vanishes and the conversion of the two reactants also decreases very much. In these conditions, a different reaction

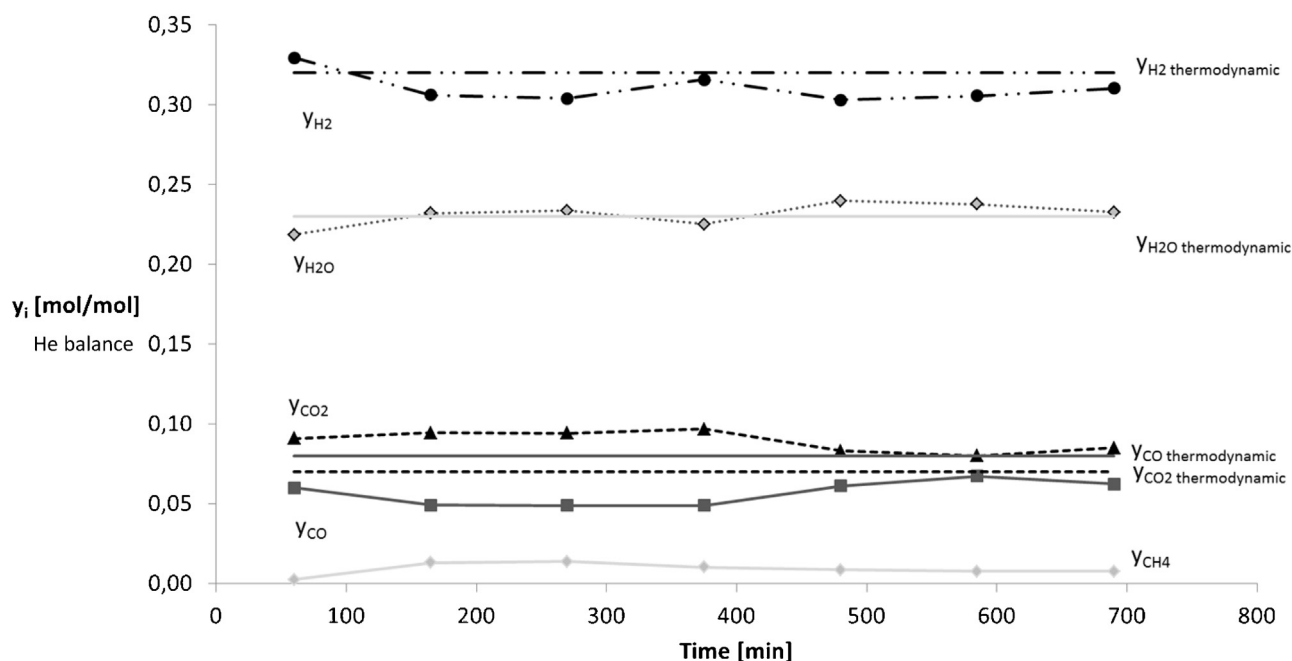


Fig. 6. Gas composition (mol/mol), as a function of the time on stream for the conversion of ethanol-phenol mixture over Ni16S700, compared with the expected equilibrium composition coming from thermodynamic calculation.

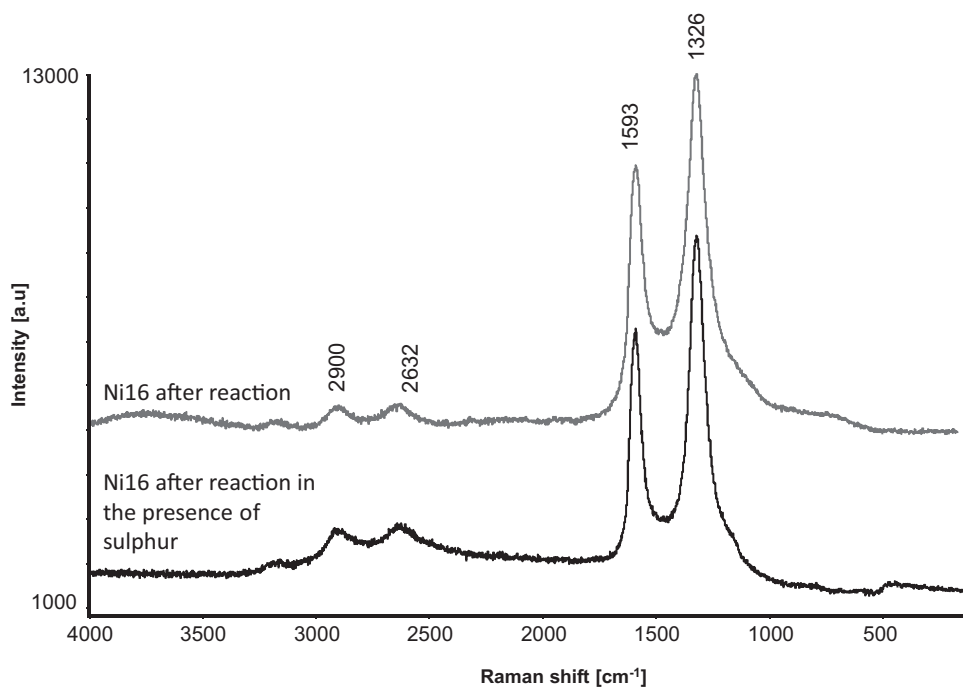


Fig. 7. Raman spectra of spent Ni16S700 catalyst after reaction in the presence and in the absence of sulphur.

Table 3

Reactants conversions (X), hydrogen yields (Y) and product carbon selectivities (S) in methanol/phenol/steam conversion over Ni39P800.

T furnace [K]	C conversion	X CH ₄ O	X C ₆ H ₆ O	X H ₂ O	Y H ₂	S CH ₄	S CO	S CO ₂	S C ₂ H ₄	S C ₂ H ₆	S C ₂ H ₆ O (DME)	S C ₄	S C ₇	S C ₈	S C ₁₀	S C ₁₂
773	0.97	0.97	1.00	-0.18	0.26	0.08	0.14	0.17	0.03	0.01	0.03	0.02	0.00	0.00	0	0.51
873	0.69	0.67	0.76	0.15	0.40	0.04	0.46	0.28	0	0.00	0.05	0.00	0.15	0.02	0.00	0
973	1.00	1.00	1.00	0.50	0.81	0.01	0.52	0.48	0	0	0.00	0.00	0	0	0	0
1073	1.00	1.00	1.00	0.46	0.79	0.00	0.59	0.41	0	0	0.00	0.00	0	0	0	0

of the two molecules occurs giving rise to anisole. Additionally, methanol is also converted to dimethylether by condensation,

to formaldehyde by dehydrogenation and some decomposition/steam reforming of methanol also occurs producing CO, CO₂,

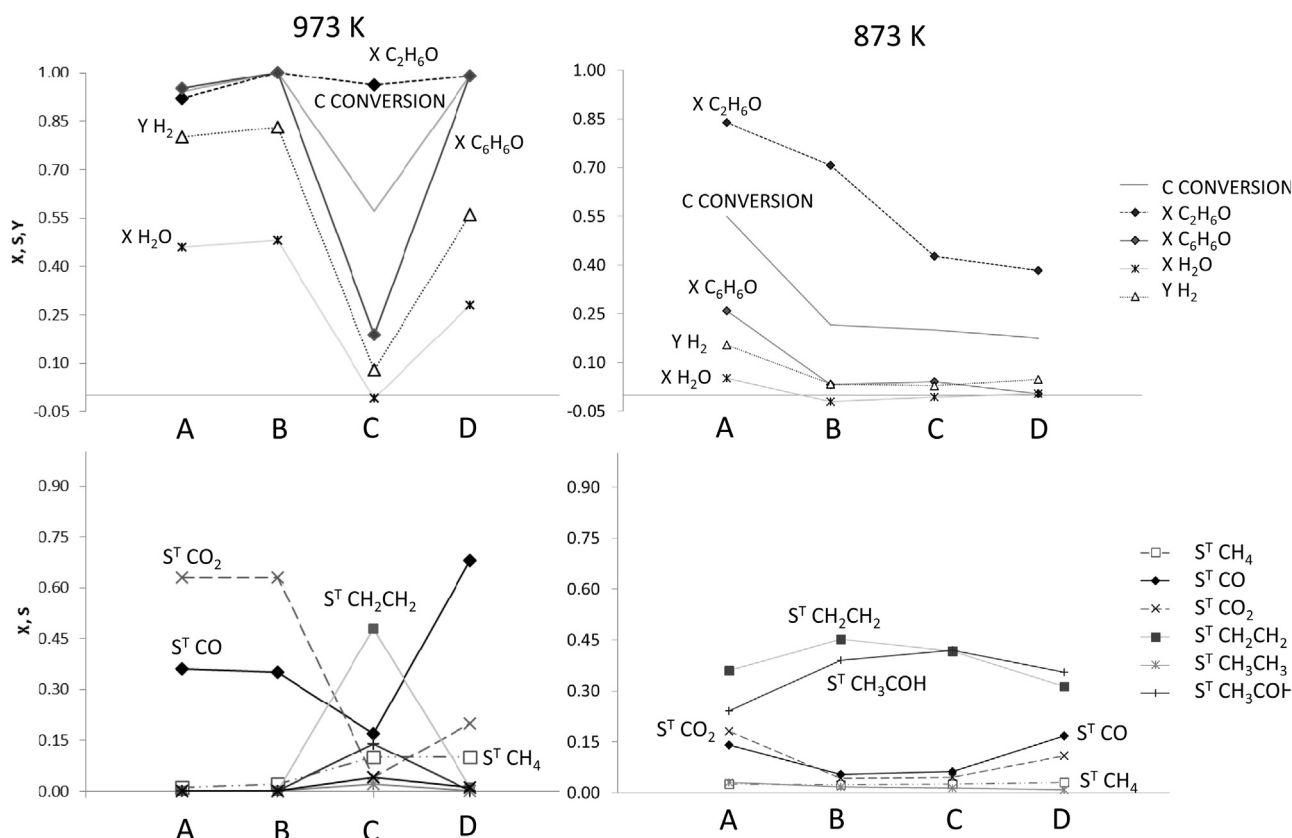


Fig. 8. Reactants conversions, hydrogen yield (Y_{H_2}) and carbon selectivities (S^T_i) to products upon pulse sulphur addition experiments on Ni16S700 catalyst at 973 K (left side) and 873 K (right side). A) No sulphur, B) after 30 min from injection of 0.011 mol_S/mol_{Ni}, C) after 30 min from injection of 0.033 mol_S/mol_{Ni}, D) after 135 min.

hydrogen and some methane. By further increasing reaction temperature, steam reforming of both phenol and methanol becomes largely the main reaction with total conversion at 1023 K and above.

When the same reaction is performed over the Ni39P800 catalyst (Table 3), the formation of hexamethyl-benzene is again very pronounced at 773 K with anisole as a main byproduct, and *para*-xylene also present as a secondary byproduct. However, according to the more easy reducibility of this catalyst (richer in Nickel) and the larger amount of metallic Nickel [35], steam reforming of both molecules is already total at 973 K with >80% hydrogen yield. In Table 4 the data obtained experimentally are compared with those calculated from thermodynamics at 973 K and 1023 K. Also in this case we have excess of CO₂ and defect of CO with respect to thermodynamics, that forecast total conversion of the reactants and essentially no methane formation.

The data obtained at low temperature indicate that the reactivity of methanol with phenol is definitely more pronounced than that of ethanol. C-alkylation occurs giving rise to the completely methylated compound hexamethylbenzene, while O-alkylation to anisole is also observed. In this case, the reaction is evident at 773 and 873 K, when steam reforming is still slow or not occurring, while it vanishes at higher temperature. It must be remarked, however that hexamethylbenzene is a low volatility molecule, also being possibly classified as a tertiary tar.

Indeed, upon methanol/phenol experiments, a clog is observed depositing in the cool section of the plant. The presence of this deposit is sometimes observed in parallel to an increase of the pressure at the top of the reactor. It is supposed that this clogging effect results in pressure drop. The IR analysis of the clog is reported in Fig. 9, where is compared to the literature spectrum of hexamethylbenzene. It is evident that hexamethylbenzene is a main component of the clog. In effect literature data report high

melting point (438 K) and boiling point (538 K) for this compound. Also in this case a number of additional compounds can be found among products at low concentration, whose structure is reported in Fig. 10. Some of them can arise from methanol only, others are due to phenol multiple methylation.

3.5. Methanol/naphthalene/steam conversion

The experiments of conversion of methanol and naphthalene in the presence of steam have been performed on the Ni16P800 and Ni39P800 catalysts, too. No evidence of reaction between methanol and naphthalene is found. On the Ni16P800 catalyst (Table 5), naphthalene conversion is very low up to 1023 K. Only at 1073 K both methanol and naphthalene are completely steam reformed with small amounts of methane production. In contrast, over the Ni39P800 catalyst, both molecules are partially converted into CO, CO₂, hydrogen and small amounts of methane already at 773 K, and completely steam reformed at 873 K and above. A comparison of the data concerning methanol/phenol and methanol/naphthalene steam reforming is not easy because of the much lower concentration of naphthalene fed, with respect to phenol. However, it seems that over Ni39P800 naphthalene is more easily steam reformed (full conversion at 873 K) than phenol (full conversion only at 973 K), while on the Ni16P800 catalyst both molecules are significantly but uncompletely steam reformed at 973 K. This may suggest that steam reforming of naphthalene (an aromatic hydrocarbon) involves extended Ni metal particles more abundant on Ni39P800, while for phenol conversion (an acidic oxygenated compound) a role can be played by the acido-basicity of the support surface, more abundant on Ni16P800.

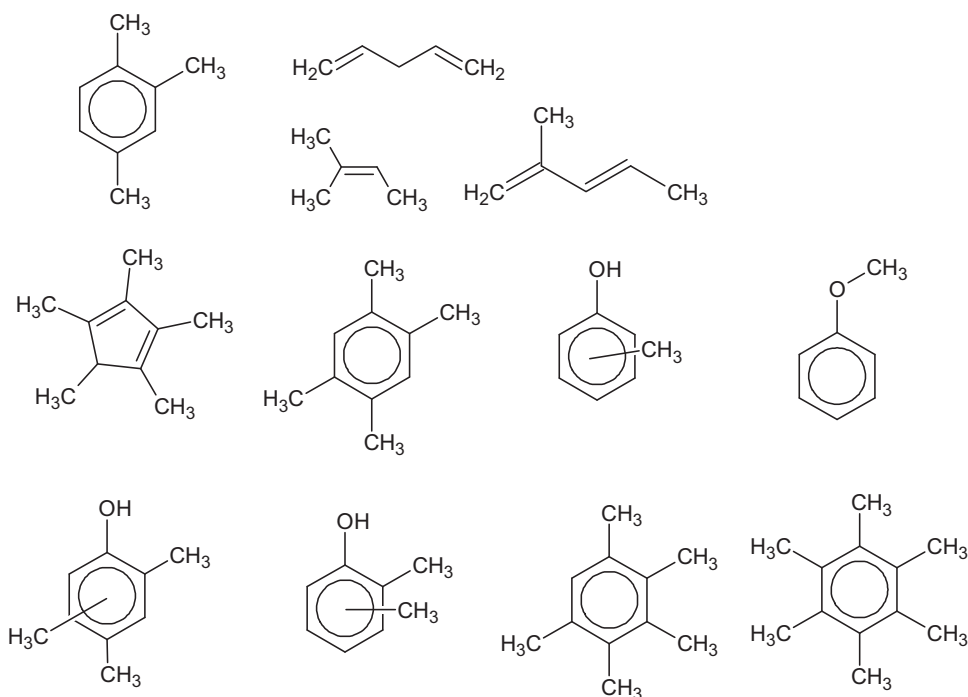


Fig. 10. Scheme of the alkylation products found at low reaction temperature by feeding methanol/phenol/water and methanol/phenol/naphthalene/water mixtures.

Table 8

Thermodynamic equilibrium displacement for methanol/phenol/naphthalene mixture and experimental compositions obtained on Ni39P800 and Ni16P800 at 973 K.

Components	Feed composition	Thermodynamic equilibrium composition (973 K)	Experimental composition on Ni39P800 (973 K)	Experimental composition on Ni16P800 (973 K)
He	0.735	0.597	0.598	0.597
CH ₄	0.000	0.001	0.000	0.001
CH ₄ O	0.095	0.000	0.000	0.000
DME	0.000	0.000	0.000	0.000
CO ₂	0.000	0.035	0.052	0.051
CO	0.000	0.067	0.050	0.051
C ₆ H ₆ O	0.005	0.000	0.000	0.000
C ₆ H ₆	0.000	0.000	0.000	0.000
C ₁₀ H ₈	1.68E-04	0.000	0.000	0.000
H ₂	0.000	0.222	0.239	0.238
H ₂ O	0.164	0.077	0.061	0.062

3.6. Methanol/phenol/naphthalene/steam conversion

When the feed contains methanol, phenol and naphthalene (Table 6) with steam, on the Ni16P800 catalyst complete steam reforming is obtained at 973 K and above with hydrogen yield >80% and no significant production of methane. At 773 K the methylation of phenol to hexamethylbenzene is largely predominant (and this caused the formation of clog, Fig. 9 and as a consequence a pressure drop) while the conversion of naphthalene is very low. If reaction is performed at 873 K hexamethylbenzene is no more formed, but conversion of naphthalene is still very low.

On Ni39P800 catalyst (Table 7) the situation is similar, with very low naphthalene conversion and big formation of hexamethylbenzene at 773 K. In this case, however, conversion of naphthalene at 873 K is significant, above 50%, while at 973 K full steam reforming is obtained. Thus, catalyst with higher Ni loading is more active also in naphthalene conversion, as expected.

As reported in [Table 8](#), at 973 K thermodynamics indeed forecasts full reactants conversion. However, again, we produce more CO₂ and hydrogen and less CO than equilibrium.

The comparison of the data in [Tables 6 and 7](#) with those in [Table 5](#) clearly indicates that the conversion of naphthalene is inhibited by the presence of phenol, but it seems that also the conversion of

phenol and methanol is inhibited by the presence of small amounts of naphthalene.

4. Conclusions

The data reported in the present paper give some information on the complexity of the picture concerning the catalytic reforming of biomass derived organic mixtures such as tar mixtures, bio-oils, bioethanol, etc. It is evident that the presence of compounds with different functionalities and volatilities, together with possible variations in reaction conditions (in particular temperature), may give rise to very complex situations. In particular, it is evident that

1. near monolayer Ni/Al₂O₃ catalysts are active for ethanol steam reforming at 973 K, and at 873 K after conditioning in reaction conditions at higher temperature. The hydrogen yield is limited by the formation of methane and CO. After conditioning in reaction conditions at high temperature, the hydrogen yield may improve, methane production dropping essentially to zero.

- The co-presence of phenol inhibits the steam reforming of ethanol at 873 K and below, favouring competitive reactions such as dehydration and dehydrogenation.
- In any case, near monolayer Ni/Al₂O₃ catalysts are active for the full steam reforming of ethanol-phenol mixture at 973 K with very high hydrogen yield. In spite of the evident production of carbonaceous materials, the catalysts do not deactivate in one-day laboratory experiments, fully converting ethanol/phenol mixture to SR products at least up to 11 h on stream.
- The catalyst tolerates very small amounts of sulphur but is significantly deactivated at higher sulphur levels. The catalytic activity is recovered by flowing sulphur free mixture. Sulphur deactivation of steam reforming catalysts occurs by poisoning of the Ni metal centers; as a result of sulphur deactivation, activity shifts to ethanol dehydration and dehydrogenation, as well as to phenol alkylation by ethanol.
- The ethanol-phenol mixture produces small amounts of a number of phenol C-alkylation products with carbon number up to 14, thus being active in converting primary tars into secondary and tertiary tars if contacted with the gas at relatively low temperature or when deactivated by sulphur.
- Methanol is even more reactive than ethanol towards phenol producing multiple methylation compounds with the final production of hexamethyl-benzene. This tar-like compound condenses in the cold section of the laboratory plant producing pressure drops. Anisole is also observed by O-methylation, together with smaller amounts of a number of poly-methylation products. Also some olefinic compounds are formed probably from methanol homologation.
- Steam reforming of naphthalene occurs in similar conditions as phenol steam reforming, or even better at least when Ni loading is relatively high. Methanol does not react with naphthalene.
- The co-presence of phenol and naphthalene seems to result in a slight mutual inhibition of their respective steam reforming processes.
- Upon steam reforming of these molecules with low times on stream, more CO₂ and hydrogen and less CO than expected by thermodynamics are usually observed, showing that water gas shift equilibrium is not fulfilled, being CO₂ the primary product of the reaction. However, at higher times on stream the equilibrium is reached, suggesting that the catalysts activates on stream for the reverse water gas shift reaction.

The main conclusion of this work is that the Ni-alumina based steam reforming catalysts are effective for steam reforming of phenol and naphthalene even mixed each other and with light alcohols at $T \geq 873$ K in the conditions of the present study in the absence of sulphur. However, at lower temperatures and when deactivated by sulphur they may become active catalysts in converting these molecules in even more heavy molecules, such as polyalkylphenols. This may be a problem when the steam reforming bed downstream the gasifier is used in non-stationary conditions, as upon shut-down and start-up procedures or even when the gasifier undergoes limited activity and temperature oscillations. This must be taken into account when such catalysts are put in the same gasifier, as gasification and steam reforming catalysts. In this case the temperature may be not homogeneously distributed in the reactor. In the coldest reactor points, the catalyst (as such or, even more, when sulphur deactivated) may play the negative role of catalyzing the forma-

tion of secondary and tertiary tar compounds from primary ones instead of reforming them.

Acknowledgements

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